



Safety and capacity retention of lithium ion cells after long periods of storage

S. TOBISHIMA^{1*}, J. YAMAKI² and T. HIRAI³

¹NTT Telecommunications Energy Laboratories, Tokai-mura, Ibaraki-ken, 319-1193, Japan;

²Institute of Advanced Material Study, Kyushu University, Kasuga Koen 6-1, Kasuga 816-8580, Japan;

³NTT Telecommunications Energy Laboratories, 3-9-11 Musashino-shi, Tokyo, 180-8585, Japan

(*author for correspondence, e-mail: tobi@iba.iecl.ntt.co.jp)

Received 17 August 1999; accepted in revised form 23 November 1999

Key words: lithium ion cell, rechargeable cell, safety, uninterrupted power supply

Abstract

This paper provides the results of simple preliminary tests on the storage characteristics of lithium ion cells in relation to their use for UPS or BPS. Commercial cylindrical 18 650 size cells with a discharge capacity of around 1200 mAh were used in the experiments. The cells consisted of an amorphous carbon anode, a LiCoO₂ cathode and an organic electrolyte. Cells were stored for 1–12 months and then their capacity was measured after constant voltage charging (similar to trickle charging) at 4.1 or 4.2 V and 21 or 60 °C. After measuring the capacity, the cells were crushed with a round 15 mm bar in diameter as an example of a fundamental abuse test. The residual cell capacity after 10 years of 4.2 V constant charging at 20 °C was predicted to be approximately 65%. This exceeds our tentative target of 50%. We also found that no cells smoked, ignited or exploded when crushed. We also measured the cell capacity after simple storage (i.e., after self-discharge).

1. Introduction

Lead–acid batteries, nickel–cadmium or nickel–metal hydride cells are generally used for uninterrupted power supplies (UPS) or backup power supplies (BPS). However, such equipment requires a new type of cell which can supply a higher energy density and provide higher capacity retention than these cells for long storage periods exceeding 10 years. Lithium ion cells are already well known as high energy density cells. They are widely used for cellular phones and video camcorders. With this kind of equipment, lithium ion cells generally experience more than 500 cycles of full charging and discharging. However, as their capacity retention when stored for long periods is unknown, it is not clear whether lithium ion cells can be used for backup power supplies. The safety of these cells when used for this purpose is also unclear and this important issue must be investigated from a practical point of view [1].

This report provides the results of simple preliminary tests on the storage characteristics of lithium ion cells in relation to their use for UPS or BPS. We used commercially available cylindrical 18 650 size (18 mm dia. × 65 mm length) cells with a discharge capacity of around 1200 mAh for the experiments. This capacity is lower than that of the cells that have been suggested for practical UPS or BPS applications. These cells consist of an amorphous carbon anode, a LiCoO₂ cathode and

an organic electrolyte composed of mixed solvents of cyclic carbonate/chain-structured dialkylcarbonate with LiPF₆ as the solute. The standard charging voltage for these cells recommended by the manufacturer is 4.2 V for general use. We measured the cell capacity after 1–12 months storage by constant voltage charging at 4.1 V or 4.2 V, and at 20 or 60 °C. After measuring the capacity, the cells were crushed with a round bar 15 mm in diameter as a fundamental abuse test for UPS or BPS application. We also measured the capacity retention by self-discharge as a reference test. The tentative target and the test conditions for this work are shown in Table 1. The tentative target was (i) more than 50% capacity retention at 20 °C after ten years storage, and (ii) no crush induced fire or explosion.

2. Experimental details

2.1. Measurement of capacity

The cell conditions before we undertook capacity measurements are summarized in Table 1. The cells were stored for 1–12 months and during this time they were charged at a constant voltage and kept at a constant temperature of 20 or 60 °C in an oven. The cell capacities were then measured galvanostatically by discharging them at 1.0 A to 3.0 V at each storage

Table 1. Test conditions and tentative targets

| Tests | Test conditions | Tentative targets |
|--------------------|--|--|
| Capacity retention | 1. Constant voltage charging (trickle charging) 1.1 Storage temperature: 20 or 60 °C 1.2 Charge voltage: 4.1 or 4.2 V 1.3 Discharge: 1.0 A to 3 V 1.4 Storage period: 1–12 months 2. Simple standing (*) (reference test) 2.1 Storage temperature: 20 or 60 °C 2.2 Discharge: 1.0 A to 3 V 2.3 Storage period: 1–12 months | 50% capacity retention after 10 years storage at 20 °C |
| Safety | 1. Crushing with round bar (15 mm diameter) 2. Heating tests for fresh cells (reference test) | No fire, no explosion Determining thermal stability limit |

* Cell capacity was also measured for the self-discharged cells after charging at 0.7 A to 4.2 V followed by 4.2 V constant voltage charging

temperature at which UPS or BPS will be used and 60 °C is the likely maximum atmospheric temperature. The cells were charged in the oven with a constant 0.7 A current to 4.1 or 4.2 V and then charged at a constant 4.1 or 4.2 V. The minimum charging current that our charger can control is 1 mA. When the charging current becomes less than 1 mA, the charging temporarily stops until the charging current flows more than 1 mA again after the self-discharge. Before storing the cells we measured their initial cell capacity by the following standard charging procedure. First, the cells were charged at a constant current of 0.7 A to 4.1 or 4.2 V, and then charged at a constant voltage of 4.1 or 4.2 V for 3 h. As a reference test, we also measured the capacity after simply leaving the cells to stand, that is, after self-discharge, at 20 or 60 °C for 1–12 months. In these reference tests, we also measured the recovered capacity of the self-discharged cells by using the standard charging procedure at 4.2 V.

2.2. Abuse tests

As a fundamental safety test to determine the suitability of these cells for UPS or BPS use, we carried out crush tests on cells that had been stored for a long time. We performed these tests at 20 °C using a round bar (15 mm dia.) and a hydraulic press that operated at a speed of 2.5 cm s⁻¹. We also carried out heating tests on fresh cells as reference abuse tests to ascertain their thermal stability [1–4]. These tests were carried out by placing the cells in an oven. First, the temperature was raised from room temperature to the predetermined level at a rate of 5 °C min⁻¹ and then held constant. In this test, the heating temperature was varied in 5 °C steps, and the constant temperatures were held until the cell temperature started to decrease. We held the temperatures for a standard duration of 3 h. We define the thermal stability limit of the cell as the highest temperature at which the cell does not smoke. In these abuse tests, we also recorded the atmospheric temperature, the cell skin temperature and the cell voltage.

3. Results and discussion

3.1. Capacity retention after constant voltage charging

The initial capacity of the cells before they were stored (fresh cells) was measured by using a 1 A constant current discharge to 3.0 V. Before discharge, the cells were charged by the standard procedure. The initial cell capacity with 4.1 and 4.2 V charging at 20 °C was 960 and 1200 mAh, respectively. The cell capacity with 4.1 V charging was 80% that at 4.2 V charging. These capacity with 4.1 and 4.2 V charging at 60 °C was 1000 and 1250 mAh, respectively.

Figure 1 and Table 2 show the cell capacity retention after the constant voltage charging. In Figure 1, 100% capacity is the initial cell capacity before they were stored. The cells were charged by the standard procedure at the same temperature as each storage temperature. None of the cells tested here were capable of completely retaining their initial capacity after storage.

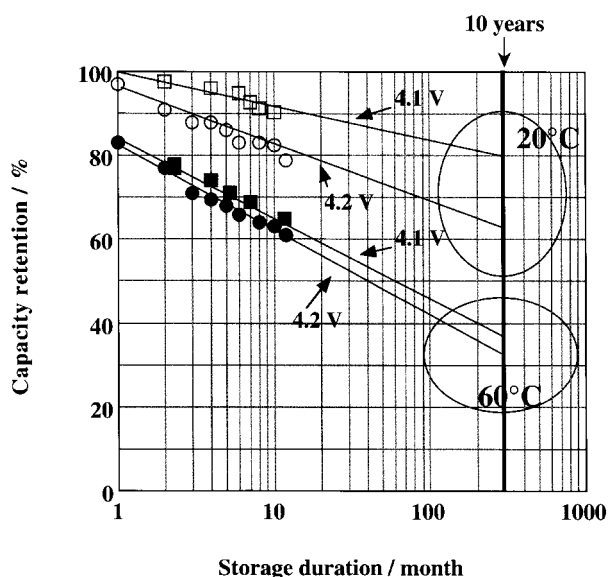


Fig. 1. Cell capacity retention when cells are stored at a constant voltage charging.

Table 2. Predicted capacity retention after 10 years storage

| Charging voltage /V | Charging temperature /°C | Capacity retention* /% | Capacity retention† /% |
|------------------------|-----------------------------|---------------------------|---------------------------|
| 4.2 | 20 | 64 | 65 |
| 4.2 | 60 | 33 | – |
| 4.1 | 20 | 80 (64 [‡]) | 83 (66 [‡]) |
| 4.1 | 60 | 37 (30 [‡]) | – |

*Predicted from extrapolated value in Figure 3

†Predicted by accelerated method [5]

‡Values vs 4.2 V charging capacity as 100%

As shown in Figure 1 and Table 2, the capacity degradation exhibited three distinct tendencies. The capacity retention decreased (i) with an increase in the storage temperature, (ii) with an increase in the charging voltage, and (iii) with an increase in the storage duration. We predicted the capacity retention after 10 years storage by two methods. With the first we used an extrapolated value corresponding to that after 10 years storage as shown in Figure 1. The second approach involves using the accelerated method established for predicting self-discharge in primary lithium metal cells [5]. With this method, the capacity retention during storage at 60 °C for 20 days is assumed to be equal to that at 20 °C for a year [5]. The capacity retention with 4.2 V charging after 10 years at 20 °C is predicted to be 64% by the first method and 65% by the second method. Both values exceed our tentative target of 50%. For 10 years storage, the capacity retention with 4.1 V charging is 80% (first method) and 83% (second method). This is approximately the same capacity as that with 4.2 V charging because the absolute capacity with 4.1 V charging is 80% of that at 4.2 V (i.e., $80\% \times 80\% \equiv 64\%$). Since the degree to which the capacity decreases with 4.2 V charging is larger than that at 4.1 V, the capacity at 4.1 V will be larger than that at 4.2 V when the storage duration exceeds 10 years.

Three possible reasons are generally suggested for the larger decrease in the capacity with an increase in a charging voltage and with an increase in the storage temperature. They are (i) cathode degradation, (ii) a carbon–electrolyte reaction on the carbon (electrolyte reduction) and (iii) electrolyte oxidation on the cathode:

- (i) The first possibility is the degradation of LiCoO_2 . As lithium is removed from LiCoO_2 , Co^{3+} is oxidized to Co^{4+} , which is known to be an unstable oxidation state. When 0.5 Li is removed from LiCoO_2 , its stability decreases greatly because the phase transition from hexagonal (disordered) to monoclinic (ordered) symmetry occurs. It is suggested that $\text{Li}_{0.5}\text{CoO}_2$ (0.5 Li removed from LiCoO_2) corresponds to 4.15 V [6, 7]. The critical temperature of the order-disorder transition is reported to be a little lower than 60 °C [6].
- (ii) The second possible reason is an increase in the production of electrochemically inert lithium

resulting from the reduction of electrolyte by the anode. This reaction causes cell capacity reduction by (a) a decrease in the number of carbon for lithium insertion, and (b) the high cell impedance resulting from both the thicker surface film of the carbon anode and the decomposition of conductive electrolytes. It has already been proved by calorimetry that the electrolyte–carbon reaction accelerates with an increase in the lithium ion insertion (with an increase in the charging voltage) and with an increase in temperature [8].

- (iii) The third possible reason is the oxidation of the electrolyte on the cathode caused by the high voltage retention. Calorimetry experiments have shown that the electrolyte–cathode exothermic reaction is stronger with a decrease in x in Li_xCoO_2 (with an increase in the charging voltage) [7]. The oxidation potential of the electrolyte becomes lower with an increase in the temperature, thus causing a stronger reaction.

Unfortunately, it is difficult to provide a reliable discussion of the capacity reduction mechanism here because we lack both the exact cell chemistry, and chemical physical analysis data on the cathode, anode and electrolytes before and after cell storage. However, reasons must be found individually for each lithium ion cell system tested because each lithium ion cell has a different chemistry, that is, different carbon, cathode and electrolyte materials. These are topics for future work.

3.2. Abuse tests for cells after being stored with constant voltage charging

Another important factor to be examined is the safety of lithium ion cells when used for UPS or BPS. Lithium ion cells may smoke when abused and can ignite when the abuse is extreme [1]. Several exothermic reactions occur inside a cell as its temperature increases. It is generally considered that ‘thermal runaway’ occurs if heat output exceeds thermal diffusion. The possible exothermic reactions are: chemical reduction of the electrolyte by the anode, thermal decomposition of the electrolyte, the oxidation of the electrolyte on the cathode, the thermal decomposition of the anode, and thermal decomposition of the cathode [1–4]. In this final case, a high voltage metal oxide cathode releases oxygen at elevated temperatures. It should also be noted that, when a separator melts as a result of the temperature exceeding its melting point (~ 125 °C for polyethylene), this frequently triggers a large heat output induced by an internal short.

Discussion is already under way on the cell safety for the cycling use [1–4]. However, the safety of cells used for UPS or BPS has not yet been sufficiently examined. Cell safety can only be determined after many kinds of tests on a large number of cells under practical conditions. However, here we have chosen the crush test as a fundamental abuse test as our aim is to obtain basic information in relation to UPS application.

We performed crush tests with a round bar (15 mm dia.) on cells stored at 4.2 V charging. In the UL 1642 standard (Underwriters Laboratories, 3rd edn, 1995) and the safety guideline for lithium secondary cells (Japan Battery Association, 1997), the crush test is carried out with a flat plate. However, we recommend a crush test which uses a round bar. This is a harder test to pass, and the cell is crushed to less than half its original thickness. Figure 4 shows example crush test results. Figure 3 is a photograph of a cell after crushing. No explosion or fire occurred. These results satisfy our tentative target. There was no distinct difference between storage at 20 °C or 60 °C as regards the maximum cell skin temperature or cell behaviour. As shown in Figure 2, within a few seconds of crushing, the cell voltage suddenly dropped to 0 V because internal shorting occurred. Then, the cell skin temperature increased as a result of internal heat output caused by the chemical and electrochemical exothermic reactions which took place locally in the cells. Figure 4 shows the relationship between the maximum cell skin temperature in crush tests and the storage duration. With increases in duration, temperature or charging voltage, the surface film on the carbon should become thicker. However, after 12 months' storage, the cell voltage dropped to 0 V in the crush test, as in case of fresh cells. Many kinds of abuse tests must be undertaken to examine cell safety in more detail [1]. However, at least these crush tests have shown that there is no tendency for the safety to decrease as the storage duration increases. Moreover, these results were not because the cell we used had superior stability to commercially available lithium ion

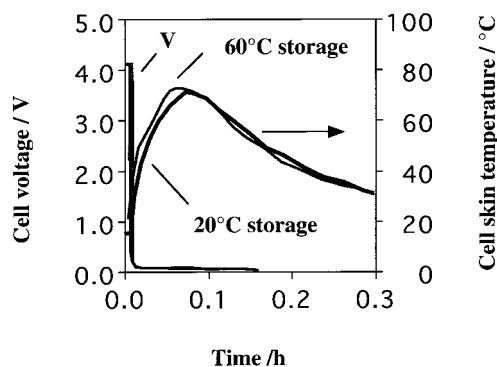


Fig. 2. Crush test results, 4.2 V charging stored for a month.

cells. Reference safety test results showing the thermal stability of the cells are described below.

Thermal stability is a basic problem as regards cell safety. A heating test to ascertain the thermal stability of a cell is one of the fundamental safety tests for lithium ion cells. Figures 5 and 6 show heating tests results for fresh cells. The cells were charged by the standard charging procedure with a charging voltage of 4.1 V (Figure 5) and 4.2 V (Figure 7). The cells charged at 4.2 V did not smoke at 155 °C but smoked at 160 °C. Therefore, we determined the thermal stability limit of these cells to be 155 °C. For many commercially available fresh lithium ion cells, this limit is above 150 °C [1], and the heating results for the cells used here are average ones. The cells charged at 4.1 V did not smoke at 170 °C but smoked at 175 °C. The thermal stability limit of these cells is 170 °C. This result is



Fig. 3. Cell after crush test, stored for 1 month at 4.2 V and 60 °C.

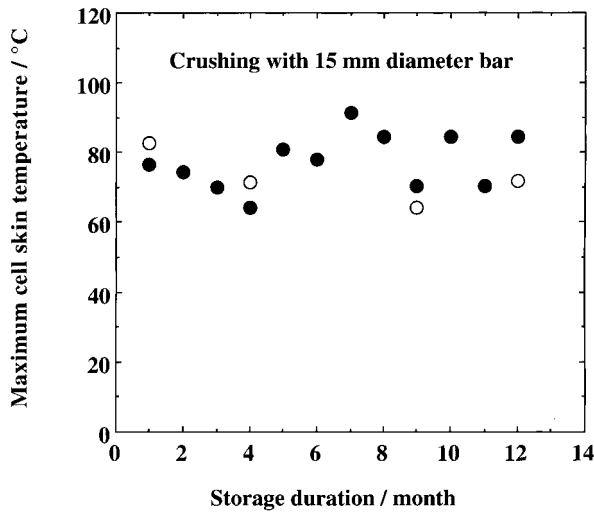


Fig. 4. Relationship between storage duration and maximum cell temperature in crush tests. Cells were stored at 4.2 V charging. Key: (●) stored at 20 °C; (○) stored at 60 °C.

obtained because the anode and cathode stability of the cells charged at 4.1 V is higher than with 4.2 V charging, owing to the 20% lower capacity of the cells charged at 4.1 V.

3.3. Self-discharge behaviour of lithium ion cells

Lithium ion cells are known to have lower self-discharge properties than nickel–metal hydride, nickel–cadmium cells or lead–acid batteries. There may be an alternative way to use lithium ion cells for UPS or BPS. That is, if the self-discharge is very low, intermittent charging, rather than trickle charging, to try to compensate for the capacity loss caused by the self-discharge. Figure 7 shows the cell capacity after self-discharge. The cells were charged at 4.2 V by the standard charging procedure before they were left to stand. The capacity recovered by charging them to 4.2 V with the standard charging procedure after self-discharge is also shown in Figure 7. After 12 months' storage at 20 °C, the cell capacity decreased to 77% of its initial value. After charging this cell, the capacity increased to 82% of its initial capacity, which is slightly larger than that obtained by trickle charging (79%). However, the capacity cannot be completely recovered by charging after self-discharge. The predicted capacity recovered after 10 years of intermittent charging at 20 °C is 57%, which is 7% lower than that obtained by trickle charging. There are three possible reasons for the capacity degradation caused by the self-discharge, and

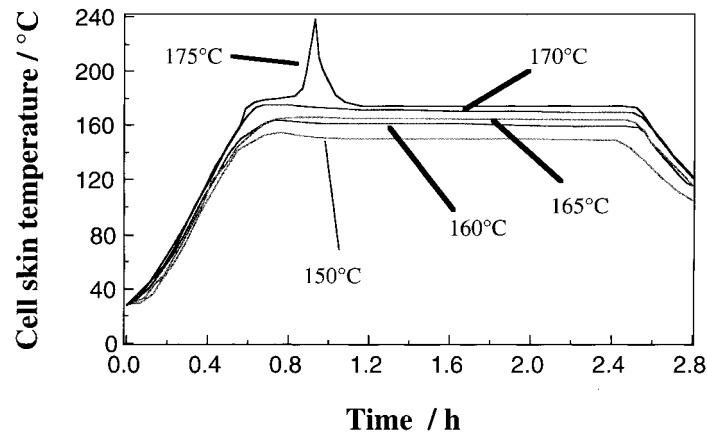


Fig. 5. Heating test results for fresh cells, 4.2 V charging.

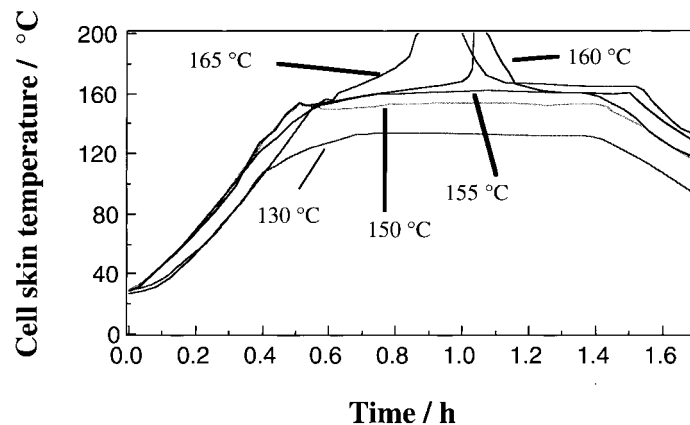


Fig. 6. Heating test results for fresh cells, 4.1 V charging.

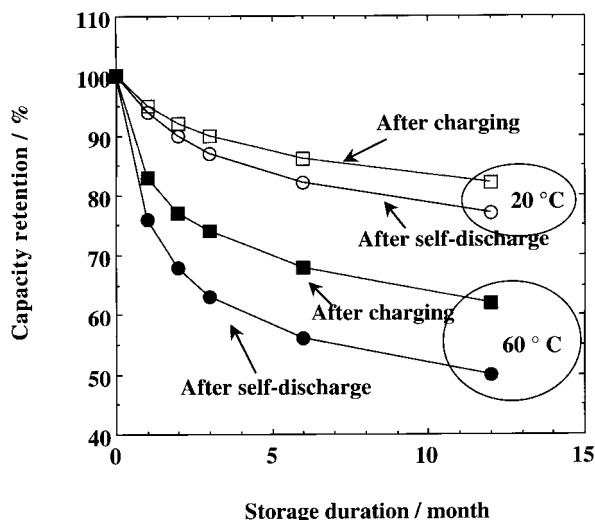


Fig. 7. Capacity after self-discharge and capacity recovered by 4.2 V charging.

they are the same as those for trickle charging. Although the carbon–electrolyte reaction may be considered a dominant factor in the self-discharge, detailed investigation must be undertaken for individual cells with different chemistries. Intermittent charging is no more effective than trickle charging. However, from a practical point of view, it is worth trying to find an alternative way to employ lithium ion cells for UPS by utilizing their self-discharge characteristics.

4. Conclusion

We carried out very limited and simple experiments to obtain basic information about the use of lithium ion cells for UPS or BPS. The experimental results obtained here give us a chance to consider the lithium ion cell as a candidate for UPS or BPS. From a practical point of view, larger capacity cells must be tested and a battery composed of multi cells must be examined in the next step. In such an investigation, cell safety and cell cost may appear as major problems to be solved. In addition, future work should include a fundamental approach to analysing the capacity degradation mechanism.

References

1. S. Tobishima and J. Yamaki, *Progress in Batteries & Battery Materials* **16** (1997) 309.
2. D.P. Wilkinson and J. Dahn, Extended Abstracts of Electrochemical Society Fall Meeting, WA, USA (1990), p. 85.
3. U. von Sacken and J.R. Dahn, Extended Abstracts of Electrochemical Society Fall Meeting, WA, USA (1990) p. 87.
4. M.A. Gee and F.C. Laman, *J. Electrochem. Soc.* **140** (1993) L53.
5. K. Inada, I. Sato, A. Miyamoto and Y. Sato, Extended Abstracts of Spring Meeting of Electrochemical Society of Japan, Osaka, Japan (1987), p. 109.
6. J.N. Reimers and J.R. Dahn, *J. Electrochem. Soc.* **139** (1992) 2091.
7. T. Ohzuku, T. Yanagawa, M. Kouguchi and A. Ueda, *J. Power Sources* **68** (1997) 131.
8. U. von Sacken, E. Nodwell, A. Sundher and J.R. Dahn, *Solid State Ionics* **69** (1994) 284.